Electronic Supplementary Material (ESI) for Materials Horizons.

Supplementary Information

Rethinking tolerance factor analysis for chalcogenide perovskites

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Table S1. List of ABS_3 materials obtained from the Materials Project[1]

Material	Crystal Structure Type	B-cation CN	Material	Crystal Structure Type	B-cation CN	Material	Crystal Structure Type	B-cation CN
$AgPS_3$	Other	4	$EuPS_3$	Other	3	$PrBS_3$	Other	3
$AgTaS_3$	Other	8	$EuZrS_3$	DP (2-4)	6	$PrErS_3$	$CeTmS_3$	6,7
$BaGeS_3$	Other	4	$GdScS_3$	DP (3-3)	6	$PrLuS_3$	$NdYbS_3$	6
$BaHfS_3$	DP (2-4)	6	$GeTiS_3$	NL	6	$PrScS_3$	DP (3-3)	6
$BaNbS_3$	Hex	6	$HgPS_3$	Other	3	$PrTmS_3$	$CeTmS_3$	6,7
$BaPS_3$	Other	3	$InAlS_3$	Hex	4	$SbCrS_3$	NL	6
$BaSnS_3$	NL	6	$InGaS_3$	Hex	4	$RbPS_3$	Other	4
$BaTaS_3$	Hex	6	$InSbS_3$	NL	6	$SmBS_3$	Other	3
$BaTeS_3$	Other	3	KPS_3	Other	4	$SmBiS_3$	Other	7
$BaTiS_3$	Hex	6	$LaCrS_3$	NL	6	$SmCrS_3$	NL	6
$BaUS_3$	DP (2-4)	6	$LaErS_3$	Other	6,7	$SmGdS_3$	Other	7
$BaVS_3$	Other	5	$LaGaS_3$	Other	4	$SmScS_3$	DP (3-3)	6
$BaZrS_3$	DP (2-4)	6	$LaHoS_3$	$CeTmS_3$	6,7	$SnGeS_3$	Other	4
$BiInS_3$	Other	6	$LaLuS_3$	DP (3-3)	6	$SnHfS_3$	NL	6
$BiSbS_3$	Other	6	$LaScS_3$	DP (3-3)	6	$SnPS_3$	Other	3
$CaHfS_3$	DP (2-4)	6	$LaTmS_3$	$CeTmS_3$	6,7	$SnZrS_3$	NL	6
$CaPS_3$	Other	3	$LaTiS_3$	NL	6	$SrHfS_3$	DP (2-4)	6
$CaZrS_3$	DP (2-4)	6	$LaVS_3$	NL	6	$SrPS_3$	Other	3
$CdPS_3$	Other	3	$LaYS_3$	$CeTmS_3$	6,7	$SrSnS_3$	NL	6
$CeBS_3$	Other	3	$MgPS_3$	Other	3	$SrZrS_3$	DP (2-4)	6
$CeCrS_3$	NL	6	$MnPS_3$	Other	3	$TbBS_3$	Other	3
$CeDyS_3$	Other	7	$MoTiS_3$	Other	6	$TbScS_3$	DP (3-3)	6
$CeErS_3$	Other	6,7	$NiPS_3$	Other	3	$ThCrS_3$	DP (4-2)	6
$CeLuS_3$	$NdYbS_3$	6	$NdBS_3$	Other	3	$TlPS_3$	Other	4
$CeScS_3$	DP (3-3)	6	$NdCrS_3$	NL	6	$TlTaS_3$	NL	6
$CeTmS_3$	$CeTmS_3$	6,7	$NdLuS_3$	$NdYbS_3$	6	$UCrS_3$	DP (4-2)	6
$CeYbS_3$	$NdYbS_3$	6	$NdScS_3$	DP (3-3)	6	$UNiS_3$	DP (4-2)	6
$CsPS_3$	Other	4	$NdTmS_3$	Other	6,7	$URhS_3$	DP (3-3)	6
$CsTaS_3$	Hex	6	$PbGeS_3$	Other	4	$UScS_3$	Other	6
$CuPS_3$	Other	4	$PbHfS_3$	NL	6	UVS_3	DP (3-3)	6
$CuTaS_3$	Other	6	$PbPS_3$	Other	3	$YScS_3$	DP (3-3)	6
$DyScS_3$	DP (3-3)	6	$PbSnS_3$	NL	6	$ZnPS_3$	Other	3
$EuGeS_3$	Other	4	$PbZrS_3$	NL	6			
$EuHfS_3$	DP (2-4)	6	$PdGeS_3$	Other	4			

Table S2. Crystal radii determined from metal sulfides[2]

Ion	Charge	CN	r^S (Å)	Data Type	Ion	Charge	CN	r^S (Å)	Data Type
Ag	+1	12	1.28	e	Ni	+2	12	1.17	e
Al	+3	6	0.69	m	Ni	+2	6	0.69	e
B	+3	6	0.5	e	P	+5	6	0.49	a
Ba	+2	12	1.73	m	P	+4	6	0.479	a
Bi	+3	12	1.63	e	Pb	+2	12	1.717	a
Bi	+3	6	1.15	m	Pd	+2	12	1.22	a
Ca	+2	12	1.56	e	Pr	+3	12	1.56	e
Cd	+2	12	1.56	e	Rb	+1	12	1.78	e
Ce	+3	12	1.602	a	Rh	+3	6	0.665	m
Cr	+3	6	0.705	m	Sb	+3	12	1.529	a
Cr	+2	6	0.9	m	Sb	+3	6	1.061	a
Cs	+1	12	2.135	a	Sc	+3	6	0.87	m
Cu	+2	12	1.34	e	Sm	+2	12	1.64	a
Dy	+3	12	1.45	e	Sm	+3	12	1.5	e
Dy	+3	6	1.03	e	Sn	+2	12	1.607	a
Er	+3	6	1.04	a	Sn	+4	6	0.86	m
Eu	+2	12	1.64	e	Sr	+2	12	1.68	e
Eu	+3	12	1.53	e	Ta	+5	6	0.75	m
Ga	+3	6	0.74	m	Ta	+4	6	0.79	m
Gd	+3	12	1.52	e	Tb	+3	12	1.51	e
Gd	+3	6	1.04	e	Te	+4	6	0.906	a
Ge	+2	12	1.4	a	Th	+4	12	1.49	e
Ge	+4	6	0.616	a	Ti	+4	6	0.73	m
Hf	+4	6	0.85	m	Ti	+3	6	0.75	m
Hg	+2	12	1.435	a	Tl	+1	12	2.17	e
Ho	+3	6	1.04	a	Tm	+3	6	1	a
In	+3	12	1.34	e	U	+3	12	1.53	e
In	+3	6	0.92	m	U	+4	12	1.45	e
K	+1	12	1.85	e	U	+4	6	0.99	m
La	+3	12	1.5	e	V	+4	6	0.66	m
Lu	+3	6	0.99	m	V	+3	6	0.72	m
Mg	+2	12	1.44	e	Y	+3	12	1.46	e
Mn	+2	12	1.485	e	Y	+3	6	1.01	m
Mo	+3	12	1.228	a	Yb	+3	6	1.02	m
Na	+1	12	1.51	e	Zn	+2	12	1.21	e
Nb	+4	6	0.77	m	Zr	+4	6	0.85	m
Nd	+3	12	1.587	a					

CN – Coordination Number; r^S – radius from sulfide data, m – measured data; e – extrapolated data; a – approximated data (data types explained below)

Table S3. Data used for extrapolated crystal radii[2]

Ion	Charge	First CN	First r^S (Å)	Second CN	Second r^S (Å)	Extrapolate CN	Extrapolated r^S (Å)
Ag	+1	4	0.92	6	1.01	12	1.28
B	+3	3	0.11	4	0.24	6	0.5
Bi	+3	5	1.07	6	1.15	12	1.63
Ca	+2	7	1.21	8	1.28	12	1.56
Cd	+2	5	0.93	6	1.02	12	1.56
Cu	+2	4	0.62	5	0.71	12	1.34
Dy	+3	7	1.1	8	1.17	12	1.45
Dy	+3	7	1.1	8	1.17	6	1.03
Eu	+2	6	1.28	8	1.4	12	1.64
Eu	+3	7	1.13	8	1.21	12	1.53
Gd	+3	7	1.12	8	1.2	12	1.52
Gd	+3	7	1.12	8	1.2	6	1.04
In	+3	5	0.85	6	0.92	12	1.34
K	+1	7	1.6	8	1.65	12	1.85
La	+3	8	1.3	9	1.35	12	1.5
Mg	+2	4	0.72	6	0.9	12	1.44
Mn	+2	4	0.725	6	0.915	12	1.485
Na	+1	5	1.16	6	1.21	12	1.51
Ni	+2	4	0.53	5	0.61	12	1.17
Ni	+2	4	0.53	5	0.61	6	0.69
Pr	+3	6	1.14	8	1.28	12	1.56
Rb	+1	7	1.73	8	1.74	12	1.78
Sm	+3	8	1.22	9	1.29	12	1.5
Sr	+2	6	1.32	8	1.44	12	1.68
Tb	+3	7	1.11	8	1.19	12	1.51
Th	+4	8	1.17	9	1.25	12	1.49
Tl	+1	6	1.45	8	1.69	12	2.17
U	+3	7	1.13	8	1.21	12	1.53
U	+4	7	1.05	8	1.13	12	1.45
Y	+3	6	1.01	8	1.16	12	1.46
Zn	+2	5	0.72	6	0.79	12	1.21

Discussion S1. Limitations of the sulfide-derived radii dataset

While the sulfide derived dataset used in this work do lead to improved predictive ability compared to the use of oxide derived data, there are still some notable limitations. Much of this data comes from Shannon's work on sulfide crystal radii.[2] The data from Shannon is based on experimental data of the crystal structures of metal sulfides (defined as measured data, m, in Table S1). Unfortunately, this work was not as extensive as Shannon's original works using oxide and fluoride data.[3,4] To fill in the gaps, linear extrapolation on other datapoints from Shannon's work was used where possible (defined as extrapolated data, e, in Table S2). Linear extrapolation has been used in recent work related to tolerance factor analysis and was applied here for simplicity.[5] However, more accurate extrapolation may be obtained using more complex, non-linear methods.[6] When linear extrapolation was not possible, the values were approximated based on bond distances of metal sulfides listed in the Materials Project database (defined as approximated data, a, in Table S1).[1] The average bond distance was used from a representative material listed above with the correct charge and coordination number. The exception to this is for Sm^{2+}, which has the same radius as Eu^{2+} when both have a coordination number of 6, so it was assumed that it also has the same radius as Eu^{2+} when both have a coordination number of 12. However, improvements and expansion of this dataset could be done with a new and in-depth analysis of sulfide material crystallographic data.

A second limitation of this dataset (and the datasets from Shannon in general) is the assumption of a constant anionic radius. Because crystallographic data only reveals bond lengths, Shannon needed to know the radius of one of the constituent ions in order to calculate the radius of the other ion. This lead to the assumption of a constant radius for the oxide anion and later to the assumption of a constant crystal radius of the sulfide anion.[2–4] But similar to how the cationic radii can vary depending on the ionic-covalent nature of the specific bond, it seems reasonable to assume that the anionic radii could also vary based on the bond nature. Therefore, more investigation is needed into how the radii of the anions is changing depending on the constituent cations.

Table S4. Comparison of computed crystal structures from Materials Project[1] and experimental crystal structures listed in ICSD for the 67 materials calculated to have octahedral structures.[7]

Material	Crystal Structure (Materials Project)[1]	Crystal Structure (ICSD)[7]	Material	Crystal Structure (Materials Project)[1]	Crystal Structure (ICSD)[7]
$AgTaS_3$	Other	Other	$LaTmS_3$	$CeTmS_3$	$CeTmS_3$ and Other
$BaHfS_3$	DP	DP	$LaTiS_3$	NL	Not Available
$BaNbS_3$	Hex	Hex	$LaVS_3$	$CeTmS_3$	Not Available
$BaSnS_3$	NL	NL	$LaYS_3$	$CeTmS_3$	$CeTmS_3$
$BaTaS_3$	Hex	Hex	$MoTiS_3$	Other	Other
$BaTeS_3$	Other	Other	$NdCrS_3$	NL	NL
$BaTiS_3$	Hex	Hex	$NdLuS_3$	$NdYS_3$	$NdYS_3$
$BaUS_3$	DP	DP	$NdScS_3$	DP	DP
$BaZrS_3$	DP	DP	$NdTmS_3$	$CeTmS_3$	$CeTmS_3$
$BiInS_3$	Other	Other	$PbHfS_3$	NL	NL
$BiSbS_3$	Other	Other	$PbSnS_3$	NL	NL
$CaHfS_3$	DP	DP	$PbZrS_3$	NL	NL
$CaZrS_3$	DP	DP	$PrErS_3$	$CeTmS_3$	$CeTmS_3$
$CeCrS_3$	NL	NL	$PrLuS_3$	$NdYS_3$	$NdYS_3$
$CeDyS_3$	Other	Other and $CeTmS_3$	$PrScS_3$	DP	DP
$CeErS_3$	Other	Other and $CeTmS_3$	$PrTmS_3$	$CeTmS_3$	$CeTmS_3$
$CeLuS_3$	$NdYbS_3$	$NdYbS_3$	$SbCrS_3$	NL	NL
$CeScS_3$	DP	DP	$SmBiS_3$	Other	Other
$CeTmS_3$	$CeTmS_3$	$CeTmS_3$ and Other	$SmCrS_3$	NL	NL
$CeYbS_3$	$NdYbS_3$	$NdYbS_3$ and Other	$SmGdS_3$	Other	Other
$CsTaS_3$	Hex	Hex	$SmScS_3$	DP	DP
$CuTaS_3$	Other	Other	$SnHfS_3$	NL	NL
$DyScS_3$	DP	DP	$SnZrS_3$	NL	NL
$EuHfS_3$	DP	DP	$SrHfS_3$	DP	DP
$EuZrS_3$	DP	DP and NL	$SrSnS_3$	NL	NL
$GdScS_3$	DP	DP	$SrZrS_3$	DP	DP and NL
$GeTiS_3$	NL	NL	$TbScS_3$	DP	DP
$InGaS_3$	Other	Other	$ThCrS_3$	DP	DP
$InSbS_3$	NL	NL	$TlTaS_3$	NL	NL
$LaCrS_3$	NL	NL	$UCrS_3$	DP	DP
$LaGaS_3$	Other	Other	$UScS_3$	Other	Other
$LaHoS_3$	$CeTmS_3$	$CeTmS_3$	UVS_3	DP	DP
$LaLuS_3$	DP	DP	$YScS_3$	DP	DP
$LaScS_3$	DP	DP			

Work Cited

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